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PROTOCOL FOR IDENTIFICATION OF REACTIVITIES OF UNKNOWN WASTES

by

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16. ABSTRACT

A test scheme (protocol) has been devised, based on standard qualitative test procedures, which will enable hazardous waste site workers to determine the gross chemical composition of waste materials. This information is used to classify wastes into reactivity groups, and thus predict compatibility characteristics.

17. KEY WORDS AND DOCUMENT ANALYSIS		
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INTRODUCTION

Under the Superfund program numerous locations have been identified containing large quantities of hazardous wastes. Uncontrolled or abandoned hazardous waste sites may not only present long-term danger to the local environment, but also possible immediate danger to personnel involved in cleanup activities. A major effort in any cleanup is the bulk recontainerization of materials residing in leaking drums or tanks, or stored in holding ponds. This is usually performed for shipment to intermediate storage or ultimate disposal. However, many materials are incompatible with each other, and when mixed can result in immediate catastrophic reactions or intermediate-term reactions that can cause dangerous results.

At present, some work has been or is being performed to identify what types of materials have compatibility problems, and the potential results of their mixing[1,2,3]. These efforts are primarily theoretical studies incorporating to chemistry of pure compounds. One study[1] has classified materials into several reactivity groups, identified potential problems with mixing different groups, and specified a logical series of procedures to avoid mixing incompatible materials. The document ("A Method for Determining the Compatibility of Hazardous Wastes") classifies wastes by chemical class and/or general reactive properties and lays out a sequence of activities to determine the compatibility of two wastes.

The key elements of this document are a compatibility chart and a flow diagram for its use. However, the aforementioned document presupposes a knowledge of the composition of the waste materials. This information is often available from generators of hazardous waste, but during remedial action at an abandoned site, it is seldom available. The need to test mix two wastes on a small scale is emphasized even if the compatibility chart indicates compatibility. Other work has been directed toward field tests for one or two specific reaction hazards or chemical characteristics[4,5,6]. These efforts address only the most immediate and catastrophic effects of incompatibility. Cleanup personnel are left with no way of estimating the short-term (minutes to hours) or long-term (days to weeks) effects of mixing and recontainerizing unknown materials.

PURPOSE

In light of the lack of comprehensive and organized field usable procedures identifying general categories of wastes, the U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory (MERL) at Cincinnati, initiated this project to identify and assemble the technology necessary to fill this void. The purpose of this project was to establish sequences of simple test procedures that would enable workers in the field to classify hazardous wastes according to their chemical reactivity when no prior knowledge was available regarding their composition. The chemical reactivity classifications (reactivity groups) would then be used to predict which waste materials could be mixed safely by applying the compatibility chart in Reference 1.

Specifically, the goals of this project were: to identify, if possible, field-usable procedures to classify wastes into the reactivity

groups developed in Reference 1; test identified procedures against representatives of their respective reactivity groups; establish a protocol for the use of the procedures; assemble a field test kit; and demonstrate the ability of the protocol and kit to function in the field.

There are 41 reactivity groups for which tests were desired. They are numbered 1 through 34 and 101 through 107 and are listed in Table 1. These are called the reactivity group numbers, or RGN's. The tests used to classify a sample waste into the correct RGN had to be simple enough so that users with minimum training could apply them. The associated protocol had to be logical and contain a minimum of complex decisions.

Because of the environment in which these classification test procedures will be utilized, there are certain desirable limitations on the schemes, test procedures, and equipment to be used. The following limitations were specifically addressed during the course of this study:

- The procedures must be safe and easy to perform by nonprofessionals. To maximize the safety of the test procedures, only small amounts of the test materials are used, and materials of extreme reactivity are identified early in the testing sequence. The simplicity of the test procedures were verified by using nonprofessionals to perform the tests in the latter part of the program.
- The procedures must give definitive, objective results. Test materials were analyzed as unknowns and by different analysts to verify objectivity of observations.

Table 1. Reactivity Group Definitions

Reactivity Group No.	Reactivity Group Name
1	Acids, mineral, nonoxidizing
2	Acids, mineral, oxidizing
3	Acids, organic
4	Alcohols and glycols
5	Aldehydes
6	Amides
7	Amines, aliphatic and aromatic
8	Azo compounds, diazo compounds, and hydrazines
9	Carbamates
10	Caustics
11	Cyanides
12	Dithiocarbomates
13	Esters
14	Ethers
15	Fluorides, inorganic
16	Hydrocarbons, aromatic
17	Halogenated organics
18	Isocyanates
19	Ketones
20	Mercaptans and other organic sulfides
21	Metals, alkali and alkaline earth, elemental and alloys
22	Metals, other elemental and alloys in the form of powders, vapors, or sponges
23	Metals, other elemental and alloys as sheets, rods, moldings, drops, etc.
24	Metals and metal compounds, toxic
25	Nitrides
26	Nitriles
27	Nitro compounds
28	Hydrocarbons, aliphatic, unsaturated
29	Hydrocarbons, aliphatic, saturated
30	Peroxides and hydroperoxides, organic
31	Phenols and cresols
32	Organophosphates, phosphothioates, phosphodithioates
33	Sulfides, inorganic
34	Epoxides
101	Combustible and flammable materials, miscellaneous
102	Explosives
103	Polymerizable compounds
104	Oxidizing agents, strong
105	Reducing agents, strong
106	Water and mixtures containing water
107	Water reactive substances

- The equipment must be standard, readily available, portable, and require minimal utility hookups, since the tests will be applied in remote field locations. For this reason, the test equipment is entirely self-contained (i.e., requires no utility hookups, etc.).
- The procedures will need to be performed as rapidly as possible, since numerous waste samples will require testing. For this reason, abbreviated classification schemes are proposed as a time-saving measure.
- The test procedures must be able to be performed with slightly restricted manual dexterity, since they may be performed in areas where protective clothing is required.
- The test procedures must be reproducible.

SCOPE

A set of 58 test compounds were selected from a listing (Appendix 1 of Reference 1) of materials likely to be found in hazardous waste disposal facilities. The compounds were selected to represent as broad a range of chemical reactivity as possible. All but one of the reactivity groups from the compatibility chart[1] is represented by the 58 test compounds.

Test procedures were identified from literature sources[7,8,9,10,11] and arranged into test schemes to classify waste materials into reactivity groups. The test procedures were applied to the 58 test compounds. In the development of the test schemes, each of the test procedures was applied to the test compounds and results were compared to those expected. The test schemes and procedures were then applied to the

58 test compounds anonymously and the results were used to classify the "unknown" test compounds into reactivity groups.

All equipment and reagents used in the test schemes were assembled into a field test kit. A manual for the use of the test schemes, including detailed instructions for conducting the test procedures and directions for use of the flow diagrams, is included in the kit.

A mixing device was assembled and was evaluated for its ability to detect reactivity by gas and heat evolution. The design of the device is a simplified version of similar devices reported earlier in the literature[11].

At the conclusion of the study, the field test kit was employed in a 1-week field evaluation at the EPA Combustion Research Test Facility located in Jefferson, Arkansas. The tests were applied to 29 "real" wastes during the field evaluation.

PROTOCOL DESCRIPTION

The protocol resulting from this project consists of 28 tests or procedures. These tests are grouped into six procedure sets which are briefly summarized in Table 2. The procedure sets are organized into a logical sequence depending on the gross physical characteristics of the sample (Figure 1). The individual tests within a procedure set are also logically organized to minimize the number of tests required for classification. Procedure set 1 is shown in Figure 2 as an example of the process.

Procedures Sequence

The test procedures are organized into a scheme for the classification of unknown hazardous wastes into reactivity groups. Preliminary procedures classify the material as acid, base, oxidizing,

Table 2. Procedure Sets

PS	Title	Information Obtained
1	pH and Redox Tests	Acidity, basicity, oxidizing and reducing potential
2	Solution-Reactivity and Special Functionality Tests	Identification of sulfides and cyanides, reactivity and solubility in acids and solvents, reactivity with water, presence of water
3	Flame Test	Combustibility, classification as organic or inorganic, identification of explosives
4	Sodium Fusion and Ferrox Tests	Identification of oxygen, nitrogen, phosphorus, sulfur, and halogen in organic waste materials
5	Organic Functionality Tests	Presence of specific organic functional groups
6	Inorganic Functionality Tests	Presence of elemental metals, heavy metal compounds, and inorganic fluorides

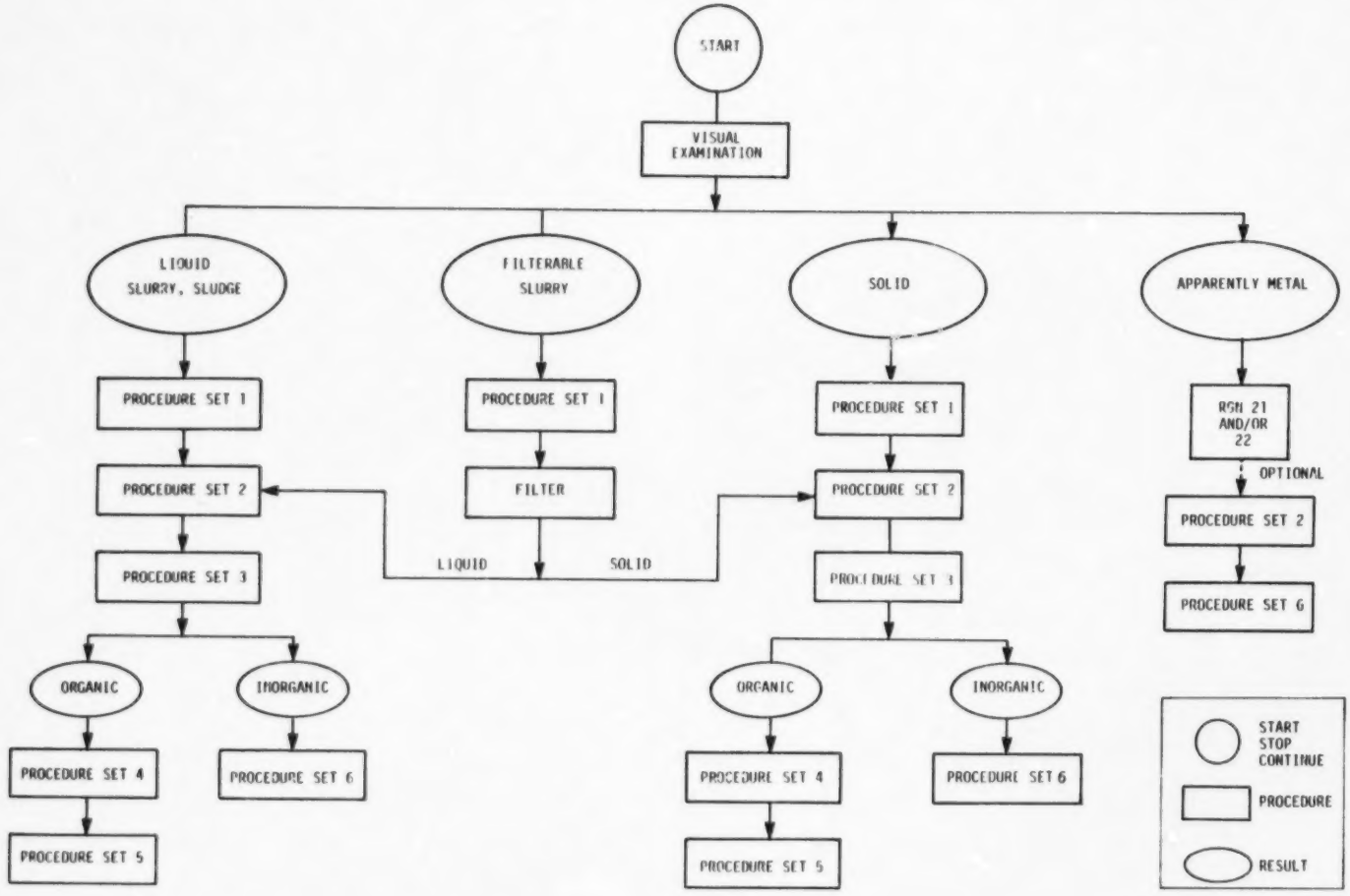

Figure 1. Sequence of Procedure Sets

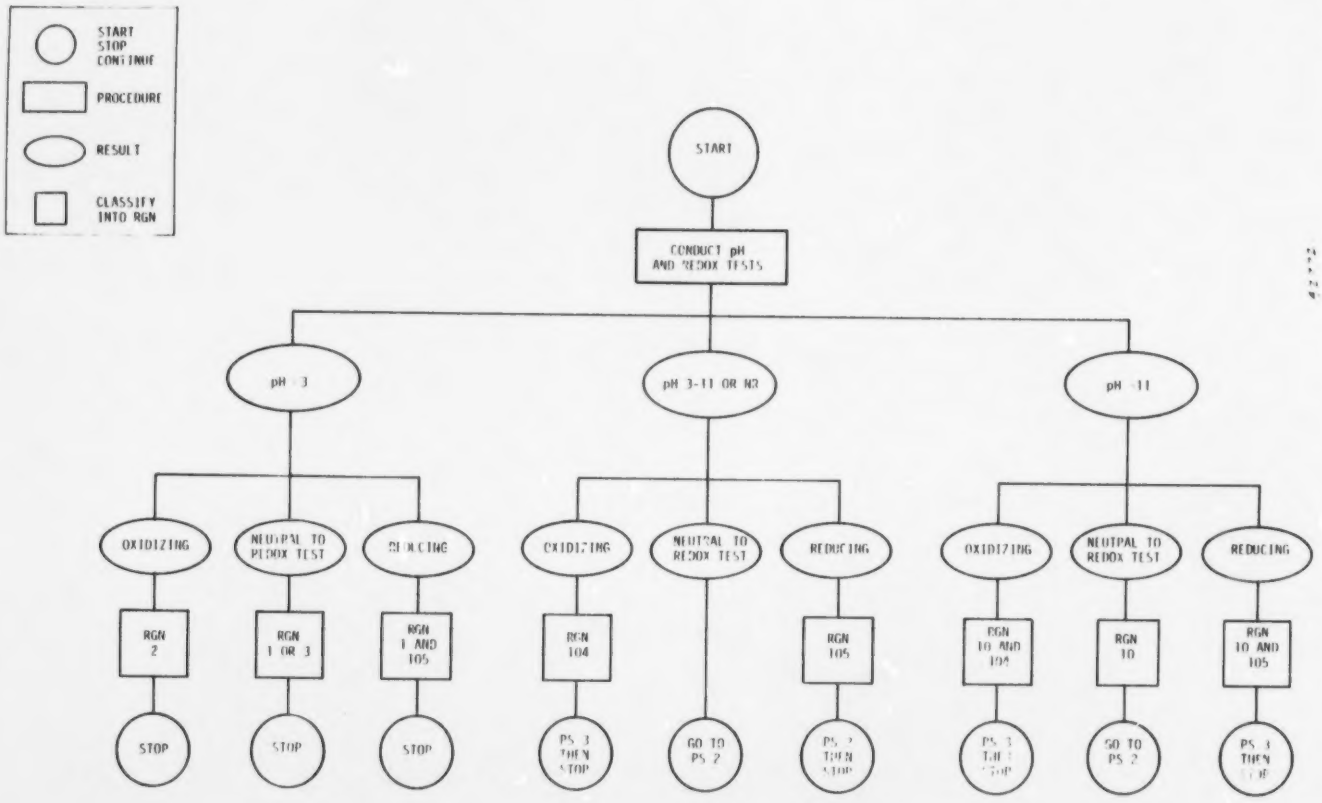

Figure 2. Procedure Set 1 -- pH and Redox Tests

reducing, or water-reactive, and primarily organic or inorganic. The results of preliminary tests are used to give direction to subsequent testing procedures which are used for further classification, ultimately into reactivity groups. The scheme is organized in a manner such that materials with high reactivity or unusual hazards are identified early in the testing sequence. In some cases, information gained in the early stages of testing can be used to classify the material and eliminate the need for further testing, or can provide cautions to be applied in subsequent testing activities (i.e., explosive hazard).

The sequence in which test procedures are carried out is shown schematically in Figure 1. The testing sequence begins with a visual examination of the waste material to classify it as a solid, sludge, slurry, or liquid. This examination may give a strong indication of its identity (i.e., metal).

Depending upon the phase of the waste material, preliminary testing is initiated. If the waste is a liquid, slurry, or sludge, PS 1 is carried out first. The rationale for beginning with PS 1 is that the chance for extreme hazards due to acidity and/or redox potential may be greater for liquids than for solids and these hazards are most easily identified. If the material is found to be strongly acidic and/or oxidative, the need for further testing is virtually eliminated (strong acids and oxidizing agents are incompatible with most other classes of wastes).

The test procedure continues with solution-reactivity tests and flame tests to determine the material's solubility/reactivity characteristics and to identify the waste as organic or inorganic. For organics, functionality tests (PS's 4 and 5) are performed to classify

the waste into specific RGN's. For inorganics, PS 6 is conducted to identify specific RGN's.

PS 1 -- pH and Redox Tests

Early in the testing sequence, pH, oxidation, and reduction tests are performed on a waste material or its aqueous solution by means of test papers. These tests identify some of the most reactive of the RGN's (those with the most limited compatibility characteristics). Specific RGN's identified are as follows:

- RGN 1 -- Nonoxidizing mineral acids
- RGN 2 -- Oxidizing mineral acids
- RGN 3 -- Orgaric acids
- RGN 10 -- Caustics
- RGN 104 -- Strong oxidizing agents
- RGN 105 -- Strong reducing agents

PS 1 is shown in Figure 2. It should be noted that classification into RGN's 1, 2, or 104 virtually eliminates the need for further testing since these RGN's are incompatible with most wastes. In addition, classification into RGN's 10 and 104 or 10 and 105 has similar consequences.

PS 2 -- Solution-Reactivity and Special Functionality Tests

This set of test procedures is conducted to determine the reactivity of the waste material with water, acids, and bases, and the solubility of the waste material in aqueous acid, base, and four organic solvents. The first procedure is the treatment of the waste material with water. At this point, most water-reactive materials are identified (and further testing is suspended). The solubility of the material in water is noted. Liquids are tested for the presence of water (RGN 106) and all waste

materials are tested for sulfide and cyanide (RGN's 33 and 11, respectively). Finally, the material is treated with an aqueous base, a series of acids, and four solvents. The following RGN's are determined in PS 2:

- RGN 11 -- Cyanides
- RGN 33 -- Inorganic sulfides
- RGN 106 -- Mixtures containing water
- RGN 107 -- Water-reactive substances

In addition, clues are given regarding the gross identity (reactive, inert, organic, inorganic) of the waste material.

PS 3 -- Flame Tests

Observation of the behavior of a material upon ignition can provide a great deal of insight regarding its composition. Results (observations) upon ignition are characterized by one of the following descriptions:

- Burns violently
- Burns (with or without smoke)
- Produces a colored flame, but does not burn
- Melts but does not burn
- Evaporates or sublimes but does not burn

While these observations are somewhat subjective, after the training period by an experienced chemist most observers will be able to make a distinction between organics, inorganics, and free metals using the flame test. RGN 107 (explosive) is determined directly by means of the flame test.

PS 4 -- Ferrox and Sodium Fusion

The classification of a material as primarily organic or inorganic is made in PS 2 or 3. PS 4 is conducted if it is determined that the material is organic, and provides elemental analysis information.

This procedure set consists primarily of two tests: sodium fusion with specific tests for nitrogen, sulfur, phosphorus, and halogen; and the ferrox test to identify organic materials containing oxygen. In addition, specific optional tests are included to differentiate between classes of hydrocarbons.

The waste material is first subjected to fusion with sodium metal. The metal is thus decomposed, and heteroatoms form sodium sulfide (sulfur), sodium cyanide (nitrogen), sodium phosphate (phosphorus) and/or sodium halide (halogen). Positive tests for sulfur, nitrogen, or phosphorus are followed by appropriate specific functional group tests (PS 6). If tests for sulfur, nitrogen, or phosphorus are negative, the ferrox test is conducted to determine the presence of oxygen. A negative ferrox test indicates the material is a halogenated hydrocarbon (RGN 17 determined by sodium fusion) or a hydrocarbon. Specific optional tests are included to distinquish between aromatics (RGN 16), alkenes (RGN 28), and alkanes (RGN 29). Since compatibility characteristics of RGN's 16, 28, and 29 are similar, it is likely that tests to distinguish these three RGN's are unnecessary.

PS 4 provides for the classification of five RGN's specifically. These are as follows:

- RGN 16 -- aromatic hydrocarbons
- RGN 17 -- halogenated organics
- RGN 28 -- unsaturated aliphatic hydrocarbons

- RGN 29 -- saturated aliphatic hydrocarbons
- RGN 32 -- organophosphates, phosphothioates, and phosphodithioates

Elemental composition information is provided which is utilized in PS 5, discussed in the following paragraphs.

PS 5 -- Organic Functionality Tests

Elemental analysis information obtained in PS 4 is used as a starting point for PS 5. This set of procedures includes specific tests for 17 reactivity groups. PS 5 contains three major parts: tests for functionalities containing sulfur, nitrogen, and/or oxygen.

If the ferrox test (PS 4) is positive, tests are conducted for functional groups containing oxygen. Three of these (RGN's 3, 30, and 34) are very reactive but information already obtained in PS's 1 and 2 is used in the classification into these RGN's. Other reactivity groups containing only oxygen (RGN's 4, 5, 13, 14, 19, and 31) are less reactive and have similar compatibility characteristics. Separate optional tests are provided for determining the presence of these RGN's, but they may be eliminated and materials with positive ferrox test placed into a composite group representing all of these RGN's.

If the sodium fusion results indicate the presence of nitrogen in the waste material, tests for functional groups containing nitrogen are conducted. Like the RGN's containing only oxygen, three RGN's (8, 9, and 18) are much more reactive than the others. Tests are therefore conducted for RGN's 8, 9 and 18 and optional tests for RGN's 6, 7, 26, and 27 are provided.

If sulfur is present (from the sodium fusion), RGN's 12 and/or 20 are indicated. These can be distinguished by individual (optional)

tests. The compatibility characteristics of these two RGN's are similar, however, and conducting tests to distinguish them is probably not necessary.

In summary, 17 RGN's are determined in PS 5:

- Oxygen functional groups
  - RGN 3 -- Organic acids
  - RGN 4 -- Alcohols and glycols
  - RGN 5 -- Aldehydes
  - RGN 13 -- Esters
  - RGN 14 -- Ethers
  - RGN 19 -- Ketones
  - RGN 31 -- Phenols and cresols
  - RGN 34 -- Epoxides
  - RGN 30 -- Peroxides
- Nitrogen functional groups
  - RGN 6 -- Amides
  - RGN 7 -- Amines
  - RGN 8 -- Azo compounds, diazo compounds, and hydrazines
  - RGN 9 -- Carbamates
  - RGN 18 -- Isocyanates (no test)
  - RGN 26 -- Nitriles
  - RGN 27 -- Organic nitro compounds
- Sulfur functional groups
  - RGN 12 -- Dithiocarbamates
  - RGN 20 -- Mercaptans and other organic sulfides

PS 6 -- Inorganic Functionality Tests

PS 6 includes tests for metals and other inorganic species not identified in PS's 1 and 2.

Solids are tested for metals using phosphomolybdic acid. The form of the metal (sheets, powder, etc.) is determined by inspection. Alkali metals are determined by their water reactivity. If the material is not an elemental metal it is dissolved (using HNO_3 if necessary). This solution (or liquid waste) is tested for the presence of heavy metal compounds (RGN 24) and for fluorides (RGN 15).

The reactivity groups determined in PS 6 are the following:

- RGN 15 -- Inorganic fluorides
- RGN 21 -- Elemental alkali and alkaline earth metals
- RGN 22 -- Elemental metals in the form of powders, vapors, or sponges
- RGN 23 -- Elemental metals in the form of sheets, rods, mouldings, drops, etc.
- RGN 24 -- Toxic metals and metal compounds

It should be noted that a test has not been identified for RGN 25, nitrides, but these compounds fit into the explosives class (RGN 102), determined in PS 2.

Determination of Compatibility

After completion of the appropriate test procedures, a waste material is classified into one or more reactivity groups, based upon the test results. At this point, the compatibility chart[1] is consulted to determine the potential effects of mixing with wastes of other classes. In cases where compatibility is indicated, wastes are mixed on a small scale.

RESULTS AND DISCUSSION

During laboratory verification of the protocol over 750 individual functionality test observations were made (PS 4, 5, and 6) on blind samples. Fifteen false positive results and two false negative results were recorded. A summary of the reliability of the test procedures employed as applied to the reference compounds is shown in Table 3. In light of the multiple functionality of many of the reference compounds, the frequency of false positive and false negative observations is considered to be acceptable.

Results of Blind Analyses of the Reference Compounds

The test schemes were evaluated by subjecting the reference compounds to the schemes. The reference compounds were submitted as unknowns after concealing their identities and assigning numbers to them. Testing was carried out following the sequence indicated in the schemes and assigning RGN's based on the individual test results.

The experimentally determined RGN's for each compound are summarized in Table 4 for the purpose of comparison with their known RGN's. Several of these compounds exhibited properties during testing which were inconsistent with their assigned RGN's (Appendix 1 of Reference 1). After evaluation of the chemical structure of these compounds, it was discovered that some of the RGN's were incorrectly assigned, and these were corrected. The RGN changes are indicated in Table 5.

Two blind test runs (A and B) were conducted by two different technicians to determine the reproducibility of the results. The second set (B) of blind analyses was carried out by a technician who was not involved in the development of the test procedures and had no specific training in chemical analysis. He was given the test kit instruction

TABLE 3. GENERAL SUMMARY OF FUNCTIONALITY TEST RESULTS

Test name	Parameter	Tests conducted	Positive results expected	False positive results	False negative results
Sodium fusion					
Cyanide/thiocyanate	Organic nitrogen compounds	40	18	0	0
Sulfide	Organic sulfur compounds	40	8	0	0
Phosphate	Organic phosphorus compounds	40	2	0	0
Halide	Organic halogen compounds	40	2	0	0
Ferrox test	Organic oxygen compounds	40	10	1	1
pH	Acids (organic)	40	3	2	0
Vanadium oxinate	Alcohols	40	3	0	0
Dinitrophenylhydrazine	Aldehydes and ketones	40	3	0	0
Schiff's test	Aldehydes	40	1	0	0
Hydroxamate	Esters	40	6	1	0
Iodine test	Ethers	40	3	6	0
Ferric chloride	Phenols	40	2	1	1
Potassium iodide-starch	Peroxides	40	2	0	0
Oxamide	Amides and/or nitriles	22	5	0	0
Dinitrochlorobenzene	Amines	22	4	1	0
Dimethylaminobenzaldehyde	Azo compounds	22	1	0	0
Glutaconic aldehyde	Hydrazines	23	1	0	0
Diphenylcarbohydrazide	Carbamates	22	1	3	0
Tetrabase fusion	Nitro compounds	22	4	0	0
Copper chloride	Dithiocarbamates	22	2	0	0
Lead acetate	Mercaptans and other organic sulfides	22	3	0	0
Baeyer's test	Unsaturated hydrocarbons	13	4	0	0
Friedel-Crafts test	Aromatic hydrocarbons	3	3	0	0
Zirconium alizarinate	Inorganic fluorides	10	5	0	0
Phosphomolybdic acid	Elemental metals	16	10	0	0
Sulfide	Heavy metal compounds	16	16	0	0
Total		755	122	15	2

TABLE 4. RESULTS OF DUPLICATE BLIND ANALYSES OF THE REFERENCE COMPOUNDS USING THE TEST SCHEMES

Compound	RGN(s)	RGN(s) (experimental) Run A	RGN(s) (experimental) Run B	Comments
Chromium oxide	2[a],24,104[a]	24,102	104,2	Reacts like explosive, color interference
Cadmium	22,24	22,24,102	22,24	Reacts like explosive
Sodium	10[f],21,102,105,107	10,102,107	--	Reacts like explosive
Arsenic pentasulfide	24[a],33	33	--	
Chromium	23,24	ND	ND	Some acid reaction, insoluble under test conditions
Copper	23,24	23,24	23,24	
Lead	23,24	23,24	23,24	
Nickel	22,24	22,24	22,24	
Barium	10,21,24[a],107	10,21,102,107	10,21,24,102,107	Reacts like explosive
Barium iodide	24[a]	ND	104	
Barium oxide	10,24[a],107[a]	10	10,22	
Calcium hypochlorite	10[f],104	10,104	10,104	
Selenium diethyl-dithiocarbamate	12,24	12	12,19	
Hydrofluorosilicic acid	1,15	1,15	1,15	
Peracetic acid	3,30[b],104[f]	3,104	3	Eliminated from scheme after PS 1
Fluoboric acid	2[f],15	2,15	2,15	
Hexafluorophosphoric acid	2[f],15	2,15	2,15	
Hydrofluoric acid	1,15	1,15	1,15	
Trinitrobenzoic acid	3[f],27,102	3	3,6/26[c]	Eliminated from scheme after PS 1
Picric acid	3,27[b],31[b],102	3,102	3,27,31	Eliminated from scheme after PS 3
Dipicrylamine	7,27,102	102	3[c],31[c]102	
Aminopropionitrile	7,26	6/26,7,14[c]	6/26,7	
Aminobenzothiazole	7	7	7,6/26[c]	
Benzoyl peroxide	30,102	13[c],30,102	30,104,102	
Cyanoacetic acid	3,26	3,6/26	3	
Toluene diisocyanate	18[d],107[a]	7[c],13[c]	9	May hydrolyze during test
Hydroxylamine·HCl	105	ND		

ND: No RGN determined

(continued)

-- Not done, insufficient sample

6/26: Same test for either RGN

[a]Not detectable by test used

[b]Not tested for this RGN due to elimination from scheme

[c]Incorrect RGN

[d]No test available for this RGN

[e]RGN not detected

[f]Corrected RGN

TABLE 4. (concluded)

Compound	RGN(s)	RGN(s) (experimental) Run A	RGN(s) (experimental) Run B	Comments
Malathion	13[f],32	3,13,32	32	pH 3
Parathion	27[e,f],32	4[c],32	27,32,6/26[c]	
Ethyl zimate	12,24	12,14[c]	12,14	
Vinyl acetate	13,103[c]	13	13	
Bromoxynil	13[e,f],17,26[e]	17	13,17,26,107[a]	
p-Chlorophenylisocyanate	17,18[d],107[a]	17	9[c],17,6/26[c]	
Styrene	16,28,103[d]	16,28	16,28	
Ethylene glycol-monomethylether	4,14[e]	4	4,14	
Polypropylene	29,101[a]	29	--	
Propyleneoxide	34[d],103[d],107	4,107	107	Hydrolyzes to alcohol
Methyl methacrylate	13,103[d]	4[c],13	13	
Ethyl acrylate	13,103[d]	13	13	
Mercaptobenzothiazole	20	7[c],20	20	
Lannate	9	9	9	
Hydroxyacetophenone	19,31	19,31	19	
Mercaptoethanol	4[e],20,105[f]	20,105	20	
b-Butylacrylate	13,103[d]	ND	13	
Acrolein	5,103[d]	5	5	
Diacetone alcohol	4[e],19	19	4,19	
Aldicarb	9	ND	17[c],32[c]	
Polysulfide	14[e,f],20,101[a],105[e,f]	3,20	20,14	
Hexene	28	28	28	
Decene	28	28	28	
Tepa	7[f],32	32	--	
Acetamide	6	6/26	6/26	
Naphthalene	16	16	16	
Diphenamide	6	ND	6/26	
n-Decane	29	29	29	

ND: No RGN determined

-- Not done, insufficient sample

6/26: Same test for either RGN

[a]Not detectable by test used

[b]Not tested for this RGN due to elimination from scheme

[c]Incorrect RGN

[d]No test available for this RGN

[e]RGN not detected

[f]Corrected RGN

manual and also a draft of this report. He was instructed in how to use the test equipment and given minimal instructions on the critical points of each test, e.g., interpretation of the flame test in terms of flammability, explosiveness, combustibility, and residue. Also some initial assistance was given in interpretation of the precipitate formation or color development for certain tests. Aside from this initial assistance, he carried all reference compounds through the test scheme and assigned RGN's without further assistance.

Potassium cyanide and dimethylaminazobenzene were not submitted to the blind tests to prevent unnecessary exposure as recommended by the Acurex safety officer. Several other compounds were also eliminated because sufficient quantities for testing were not available, as indicated in Table 4. Of the remaining reference compounds (test run A), seven were assigned incorrect RGN's or no RGN could be determined. For three of these compounds the results are explained by their chemical behavior during testing. Chromium was not detected as elemental metal because of its extreme insolubility under the test conditions. Barium iodide, barium oxide, and barium cannot be detected as barium sulfide, and toluene diisocyanate showed positive amine and ester test results, while the isocyanate group was not detected because no qualitative test method was available. Other difficulties were the detection of water reactivity (RGN 107) which was defined as reaction with visible gas evolution or spattering. This resulted in nondetection of RGN 107 for three compounds: barium oxide, toluene isocyanate, and chlorophenyl isocyanate. In addition, polymerizable compounds were not detectable. Several materials (chromium trioxide, cadmium, and barium)

reacted violently during the flame test, although they are not considered explosives.

The comparison of results from both test replicates show good correlation of most RGN's. The individual functionality tests also showed good agreement, with 18 disagreeing individual test results out of the 261 individual determinations.

Results of Blind Analyses of Other Pure Compounds

Two sets of unknown laboratory chemicals were tested by following the test scheme. Six unknowns were mixtures of two compounds (HWC-X, 1-6); twelve unknowns were single compounds (HWC-X, 11-22). The RGN's determined from testing as compared to their actual RGN's are presented in Table 5. Out of the 12 single unknown compounds tested all RGN's were correctly assigned for 9 compounds and for the remaining 3 the most significant RGN's were assigned. Four RGN's were incorrectly assigned (false positive) and one RGN was not detected. For the six unknown mixtures, the RGN's were only partially identified because several of the tests which would identify functional groups of the second component of the mixture were not conducted according to the test scheme in the following instances: (1) in the presence of certain functional groups, (2) at a specific pH (less than 3,) or (3) where the mixture exhibited explosive behavior during the flame test. Nevertheless, the most significant RGN's were assigned for all of the six mixtures.

FIELD EVALUATION OF THE PROTOCOL AND TEST KIT

A field evaluation of the test kit was conducted on March 8 through 11, 1983 at the EPA Combustion Research Facility in Jefferson, Arkansas. Twenty-five hazardous waste samples were collected from two sites prior to the field evaluation by Mr. Richard Carnes, EPA Technical Advisor for

TABLE 5. RESULTS OF BLIND ANALYSES OF SELECTED PURE COMPOUNDS AND BINARY MIXTURES

Hazardous waste combination	Compound	RGN(s) (known)	RGN(s) (experimental)
Two (2) Components			
1	Picric acid, ethylene glycol monomethyl ether	4[b],14[a],31,27[a], 102	3,102
2	Mercaptobenzothiazole diacetone alcohol	20,4[b],19,105	20,19,7,105
3	Styrene, hydroxyacetophenone	16[a],103,4,19, 31,28[d]	4,19,31,32[c],16, 28
4	Bromoxynil, vinyl acetate	17,26[b],13,103[d]	9,17,13
5	Mercaptoethanol, hexane	4,20[e],28[a]	4
6	Chlorophenyl, isocyanate	17,18[d],107[b]	17,19[c],6/26[c]
Single Compounds			
11	Iodine	104,2	104,2
12	Sodium borohydride	105	105,14[c],102,17[c]
13	Sodium diethyldithiocarbamate	12	12
14	Stannous sulfate	24,105,1	1,24,105
15	Benzoic acid	3	3,19[c]
16	Bromobenzene	17	17
17	Phenylhydrazine	8	14[c],8
18	O-Nitroaniline	7,27[b]	7
19	Pyrogallol	3,31,105	3,31,105
20	Tin (granules)	22,24	22,24
21	Biphenyl	16	16
22	Hydrofluoric acid	1,15,106	1,15,106

[a]Not tested for this RGN due to elimination from test scheme

[b]RGN not detected

[c]Incorrect RGN

[d]No test available for this RGN

the project. Four of the samples had two distinct layers. For these samples, the layers were sampled and analyzed separately, bringing the total number of samples analyzed to 29. The gross identity of the waste materials was known to the technical advisor but not to the field crew until after the testing was completed.

The tests were performed outside (day 1) on a temporary plywood working surface and in a trailer with a counter (days 2 and 3) because of inclement weather. The wind was gusting from 20 to 30 mph, and the temperature was in the mid-30's (°F). It is believed that these conditions simulated field conditions closely.

Only two significant difficulties were encountered in performing the tests under field conditions. The first was that several of the samples contained two phases and the kit was not equipped with a separatory funnel or equivalent device. Based on this experience, several small separatory funnels were added to the test kit equipment list. A second problem encountered was performing the tests under adverse weather conditions; a particular problem was wind. Under windy conditions reagent bottles and sample vials tipped over and the flame was difficult to maintain and control. Overall, the tests proved relatively easy to perform under field conditions.

A list of the samples including the composition and a summary of results is presented in Table 6. Twenty-eight of the twenty-nine samples were categorized correctly (according to the impartial judgment of the project technical advisor onsite) in the field evaluation. Sample 6E was described as "waste solvents with amines" but was characterized as RGN's 10 (caustic), 24 (metal compounds), and 106 (water). Upon contacting the source of this sample it was found that indeed we had accidentally been

TABLE 6. DESCRIPTION OF SAMPLES TESTED AND SUMMARY OF RESULTS OF THE FIELD EVALUATION

Sample[a]	Sample identification	Sample description	RGN(s)	
			Predicted	Found
1D	Dirty PCE	Yellow-brown liquid	17	4,17
2D	TCE still bottoms, oil, hydrocarbons	Dark brown emulsion very small upper layer	17	16,17
3DU	Ethanol wash and oils	Brown liquid (upper layer of two layers)	16,28	16
3DL	Ethanol wash and oils	Pale brown liquid (lower layer of two layers)	4,106	106
4DU	Toluene in thinner wash	Pale yellow liquid (upper layer of two layers)	16	16,19
4DL	Toluene in thinner wash	Pale brown liquid (lower layer of two layers)	106	106
5D	MEK, xylene, and solvents	Very light tan emulsion	16,19	4,16,19
6D	Acetone and MEK	Light purple emulsion	19	19
7D	MEK from paint manufacturing	Green-brown emulsion	19	16,19
8DU	Still bottoms from solvent recovery refinery	Dark brown slurry (upper layer of two layers)	[b]	102
8DL	Still bottoms from solvent recovery refinery	Pale yellow liquid (lower layer of two layers)	[b]	24,106
1E	Organochlorine waste streams	Very dark (opaque) viscous liquid	17	17
2E	Wastewater from storage tank	Tan liquid (very small amount of dark brown liquid on top)	106	10,24,106
3E	Waste naphtha	Light brown clear liquid	16,28, or 29	4,16,31
4E	Carbon tetrachloride	Dark brown clear liquid	17	3,16,17
5E	MIBK with waste solvents	Light pink clear liquid	19	4,19,31

[a]Sources of hazardous waste samples are being kept anonymous at the request of the project technical advisor

[b]See discussion

[c]Not well defined by waste description

[d]Also found to contain organics

[e]Water not predicted by waste description

TABLE 6. (concluded)

Sample[a]	Sample identification	Sample description	RGN(s)	
			Predicted	Found
6E[b]	Waste solvents with amines	Light brown clear liquid	7	10,24,106[b]
7E	Thiocarbohydrazide with H_2S	Red-orange clear liquid	33,105,106	10,33,105,106
8E	Spent caustic	Clear colorless viscous liquid with small amount of black particulate	10,106	10,106
9E	Ethylene dichloride still bottoms	Very dark blue liquid	17	17
10E	Waste solvents, waste ink	Dark gray viscous liquid	b	13,19
11E	Waste varnish	Light brown clear viscous liquid	16	16
12E	Water base insecticide	Milky white opaque viscous suspension	106[c]	106[d]
13EU	Oil base insecticide	Yellow clear liquid (upper layer of two layers)	d	16
13EL	Oil base insecticide	Cloudy light yellow liquid (lower layer of two layers)	d,e	106
14E	Tribromocumene	Opaque red-brown viscous suspension	16,17	16,17
15E	PCB oil, high level	Light yellow-green clear liquid	16,17	16,17
16E	PCB oil, low level	Light orange clear liquid	16,17	16
17E	Silicone oil (with PCB's)	Very light yellow-green clear liquid	16,17	16

[a]Sources of hazardous waste samples are being kept anonymous at the request of the project technical advisor

[b]See discussion

[c]Not well defined by waste description

[d]Also found to contain organics

[e]Water not predicted by waste description

given the water layer of a two-layer system. Amines dissolved in the water would account for the caustic (RGN 10) description and could act as a chelating agent to carry heavy metals into the water. Another sample, 3D, was described as ethanol wash (two layers). The upper layer was identified as aromatic hydrocarbon (RGN 16), but only water (RGN 106) was detected in the lower layer. Two oil samples containing PCB's (samples 16E and 17E) were identified only as aromatic hydrocarbons. The PCB levels in these samples was not known, but is assumed to be low (trace level) in which case the chloride was present at too low a level to be detected.

Sample 8DU was identified as organic but examination was not carried beyond the flame test. The flame test results indicated to a technician that the material might be an explosive. Further testing would have been at the discretion of a qualified supervisor. In fact, the material was the organic layer from the still bottom of a solvent recovery refinery. The lower (water) layer was found to contain metals. Thus, the flame behavior of 8DU was probably due to burning metallic materials in the sample.

Sample 3E, a waste naphtha, was found to have sulfur present but no sulfur compounds were identified. Sulfur is not uncommon in naphtha, either as elemental sulfur or as organic sulfides. Organic sulfur groups other than mercaptans, thiocarbamates, and disulfides are not detected by the methods used in the test scheme. The failure to identify sulfur-containing organic species may also indicate a difference in sensitivity between the test for sulfur and the specific functionality tests. The same conclusion can be reached from the results of sample

10E. A positive nitrogen response was obtained but no nitrogen compounds were detected in this waste sample.

A carbon tetrachloride waste sample (4E) was found to contain aromatics and organic acids as well as being in RGN 17 (chlorinated organics).

Two minor shortcomings of the test schemes were pointed out by the field evaluation. The test schemes are organized such that aqueous liquids are not tested for organics. The sodium fusion procedure, as well as a number of specific organic functionality tests are not amenable to aqueous solutions. For compatibility purposes, the classification of aqueous organics as aqueous mixtures would probably suffice. For purposes of predicting optimum destruction technology, the inability to detect organics in water may be a serious limitation.

During the field test, approximately 40 man-hours were spent in actual sample analysis. Since 29 phases were analyzed, an average analysis time of approximately 1.3 hr/sample was realized. This average analysis time is expected to be quite acceptable in real-world field applications.

CONCLUSIONS

As with any new protocol or methodology, there are areas needing further work. For the protocol as it relates specifically to the RGN classification system put forward in Simmons, et al.[1], there are four RGN's for which specific class tests have not been identified. These are isocyanates, epoxides, nitrides, and polymerizable materials. Two weaknesses were found in the RGN classification system; the failure to identify at what levels a particular RGN may pose a problem, and the lack of a classification for water solutions containing high levels of soluble

organics. These weaknesses are mirrored in the current protocol in that detection limits have not been established and a procedure for identifying organics in water has not been defined. Finally, although it was originally hoped that the procedure would be so simple and so explicit that almost any technician could successfully use the kit and protocol it is recommended that users have some minimal training (circa 1 week).

The protocol and kit were used successfully to identify 28 real waste samples in the field. Specifically,

- 36 of 41 predicted RGN's were identified
- 13 unpredicted RGN's were found
- One mislabeled sample was found
- The average analytical time was 1.3 hr/phase

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REFERENCES

1. Hatayama, H. K., J. J. Chen, E. R. de Vera, R. D. Stephens, and D. L. Strom, "A Method of Determining the Compatibility of Hazardous Wastes," EPA/600/2-80-076, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1980.

2. Lynn, J. P. and H. E. Rossow, "Classification of Chemical Reactivity Hazards," National Technical Information Center, Alexandria, Virginia, 1970.

3. ASTM Committee D34 report in progress (personal communication: B. C. Malloy, Chairman).

4. Dahn, C. J., "Chemical Compatibility and Storage Considerations for Process Systems Hazards Analysis," Journal of Hazardous Materials, Volume 4, pp. 121-127, 1980.

5. Myers, L. C., "The Chemical Reactivity Test -- A Compatibility Screening Test for Explosives," Journal of Hazardous Materials, Volume 4, pp. 77-87, 1980.

6. Turpin, R. D., "Oxidation/Reduction Potential Field Test Kit for Use at Hazardous Material Spills," Hazardous Material Spills Conference, 1982.

7. Cheronis, N.D., and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, New York, 1960.

8. Feigl, F., "Spot Tests in Inorganic Analysis," Elsevier Publishing Company, New York, New York, 1972.

9. Feigl, F., "Spot Tests in Organic Analysis, "Elsevier Publishing Company, New York, New York, 1966.

10. Rand, H. C., A. E. Greenberg, and M. J. Taras, "Standard Methods for the Examination of Water and Wastewater," 14th ed., American Public Health Association, Washington, D.C., 1978.

11. Simmons, B. P., I. Tan, T. H. Li, R. D. Stephens, and D. L. Strom, "A Method For Determining the Reactivity of Hazardous Wastes," U.S. Environmental Protection Agency, Cincinnati, Ohio, 1982 (Preliminary).